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By Robert W. Freedman and Frederick A. Sharp

UNITED STATES DEPARTMENT OF THE INTERIOR

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BUREAU OF MINES
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DETERMINATION OF SULFATES IN DIESEL EXHAUST

By Robert W. Freedman[1] and Frederick A. Sharp[2]

ABSTRACT

This report describes sampling and analytical procedures used for measurement of sulfates in diesel tailpipes and in the diluted exhaust within dilution tunnels. A variety of methods exist for sulfate analysis for such systems, including ion exchange. Two chemical methods used by the Bureau of Mines are described in detail. These are based upon spectrophotometric measurement of chloranilic acid using barium chloranilate. The procedures are rapid and relatively inexpensive. In general, ion exchange is preferred by many analysts for sulfate analysis. However, it is more complex and expensive than chloranilic acid procedures, which are adequate for exhaust analysis.

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INTRODUCTION

Diesel fuel generally contains 0.1 to 0.5 pct S, which is converted mainly to SO_2 in the combustion process. Although several hundred parts per million (ppm) of SO_2 form in the exhaust, this is generally diluted to acceptable levels in the ambient mine atmosphere by ventilation. However, the oxidizing effect of a catalytic converter yields 50-60 pct conversion to SO_3, which is a much more toxic contaminant, as it exists in the exhaust mainly as sulfuric acid mist. The great toxicity of H_2SO_4 makes analysis important.

Several of the techniques for measuring moderately low levels of sulfates in general involve titration, spectrophotometry, flame photometry, turbidimetry, and ion exchange with conductimetric reading (8).[3] Thermal decomposition of insoluble organic derivatives, such as perimidylammonium sulfate, with flame photometric measurement (7), has been used. A recent review (13) covers the current state of analytical methodology for determining sulfate in airborne particles, including speciation or separation into H_2SO_4, ammonium, and metal sulfates.

In this publication, two chloranilate laboratory methods were modified in our laboratory and described in detail. Sampling techniques and the other methods were taken from the literature and described briefly. A two-column ion exchange method (12) was described in greater detail since many chemists favor ion exchange.

DESCRIPTION OF METHODS

The selection of methods for measuring diesel tailpipe emissions can be narrowed down to include total sulfate in solution as sulfuric acid in the concentration region of 10 to 300 ppm on a weight/volume (w/v) basis. The state-of-the-art of sulfate sampling is considerably less advanced than chemical analysis of sulfate in solution.

Sampling Problems

Sampling technology for diesel exhaust sulfate analysis requires further development, mainly because of difficulties in sampling hot gases. Parameters such as temperature, sampling flowrate, and dewpoint should be controlled in order to obtain comparable results in sampling combustion effluents (2). Sulfuric acid must be maintained above its dewpoint until it reaches the sampling point (5). To accomplish these goals, a modification of the Goksoyr-Ross controlled condensation sampling technique (4), which is also described in ASTM D3226, has been employed. In this technique, H_2SO_4 is trapped by a filter or frit as H_2SO_4, and the separated SO_2 is converted to SO_3 by absorption in Greenberg impingers (EPA Method 5)[4] or in midget impingers (EPA Method 8) containing dilute hydrogen peroxide (H_2O_2).

It is the opinion of several investigators that problems occur in all these collection procedures. For example, during collection on a filter or frit, up to 10 pct of the SO_2 can be catalytically converted to SO_3 by carbon accumulating on the surface.

Chemical Analysis

With sulfate in exhaust collected or absorbed in water or aqueous alcohol, quantitative analysis can readily be performed in the 0- to 300-ppm (w/v) range. Three reliable procedures for sulfate that can be employed are batch barium cloranilate (11), the EPA column chloranilate procedure (14), and ion exchange

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[4]U.S. Environmental Protection Agency.

using high-performance liquid chromatography (HPLC) (8, 10). In the ion exchange method, an anionic column with conductivity detection is employed to separate ions such as NO_3, Cl, and $SO_4^=$. Dow Chemical Co.[5] (12) did the research that led to the development of an automated ion chromatograph available from Dionex. High conductivity from background anionic eluant is removed by a suppressor column in the hydrogen form by formation of a weakly ionized compound (example: $Na + HCO_3 + RH^+ = RNa^+ + H_2CO_3$).

EXPERIMENTAL PROCEDURES

Collection Procedures

Collection is accomplished either by a direct stack or tailpipe sampling or by using the dilution tunnel employed for particulate sampling. The dilution tunnel is considered superior for accurate SO_3 sampling by a majority of observers.

Stack Sampling

The Ontario Research Foundation (ORF) is investigating a stack sampling system employing the Goksoyr-Ross technique (4) with controlled condensation and collection of H_2SO_4 on a medium-porosity frit, followed by trapping the gas phase and conversion of SO_2 in the presence of H_2O_2. Greenberg impingers have been substituted for midget impingers by ORF, as described in an ORF internal quarterly report (9).

Dilution Tunnel Sampling

Arthur D. Little, in a recently completed study under contract for the Bureau of Mines (6), collected SO_3 as H_2SO_4, at a flowrate of 6 lpm, as part of the total particulate collection using a small dilution tunnel at air-exhaust ratios of 5:1 to 15:1. Pallflex T60A 20-membrane filters are employed with water extraction for subsequent ion chromatographic analysis. Material balances are obtained by a separate SO_2 train in which filtered dilution tunnel exhaust is passed at a flowrate of 1 lpm through impingers containing 3 pct H_2O_2 in water.

[5]Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

Chemical Analysis

Most analysts consider the ion exchange method (3, 8, 10, 12) to be the method of choice for a wide range of concentrations. However, spectrophotometric methods using barium chloranilate are considerably simpler, less expensive, and adequate for the analysis of sulfate in exhaust gas.

Two simplified procedures, both of which employ barium chloranilate, that are adequate for tailpipe or dilution tunnel concentrations are used at the Bureau of Mines Pittsburgh Research Center. One is a batch procedure using the 530-nm absorption band, and the other is a column procedure using the 310-nm band.

Barium Chloranilate Batch Method

Barium chloranilate releases the chromophore, chloranilate ion with the formation of barium sulfate. The procedure used by the Bureau is based upon the method described by Bertolacini and Barney (1) and an improved method of Schafer (11). Absorbance of chloranilic acid at 530 nm is measured after contacting the sample with barium chloranilate adjusted to about pH 2, using a chloroacetate buffer. Analysis is conducted as follows.

Preparation of Reagents and Standards

1. Prepare an H_2SO_4 aqueous stock solution of 500 ppm (as SO_4). Add 52.1 ml of standard 0.1N H_2SO_4 to a 500-ml volumetric flask from a buret, and make up to mark.

2. Prepare aqueous SO_4 standards in the 0- to 500-ppm range by dilution of stock solution with distilled, ion-exchanged water. These standards and the unknown solutions will eventually be diluted to 5 times volume with isopropanol (i.p.) to yield approximately[6] 80 pct i.p. [volume/volume (v/v)] solvent.

3. Prepare a chloroacetate buffer, 2M, by dissolving 18.9 g $CH_2ClCOOH$ in 50 ml of H_2O and slowly adding solid NaOH, chilling the graduated beaker with ice. At a pH of about 1.5, at 25° C, finish the partial neutralization with 6N NaOH to a final pH of 1.8 to 1.9 at 25° C. Dilute to about 100 ml.

4. Shake reagent-grade barium chloranilate powder with about 10 times its volume of 80 pct i.p., filter, and air-dry. This usually lowers the blank value.

Analysis

Add about 25 mg barium chloranilate to plastic 15-ml centrifuge tubes provided with caps. Add about 5 ml i.p. and 2 drops of buffer. Prepare SO_4 standards, 0 to 500 ppm. Pipet in 2.00-ml sample of standard, dilute to the 10-ml mark with i.p., cap, and shake by hand about 200 times. Centrifuge at 3,000 to 5,000 rpm for 5 min. Pour the supernatant liquid into 1-cm cells and measure absorbance versus blank at 530 nm; repeat with unknown samples and read the concentration of SO_4 in parts per million from the calibration curve prepared from the standards. The blank should read about 0.03 versus H_2O.

Column Chloranilate Method

At the Bureau, the EPA procedure of Tejada (14) was employed with minor modification for manual operation. A schematic of Tejada's system is shown in figure 1.

[6]Alcohol and water contract slightly when mixed.

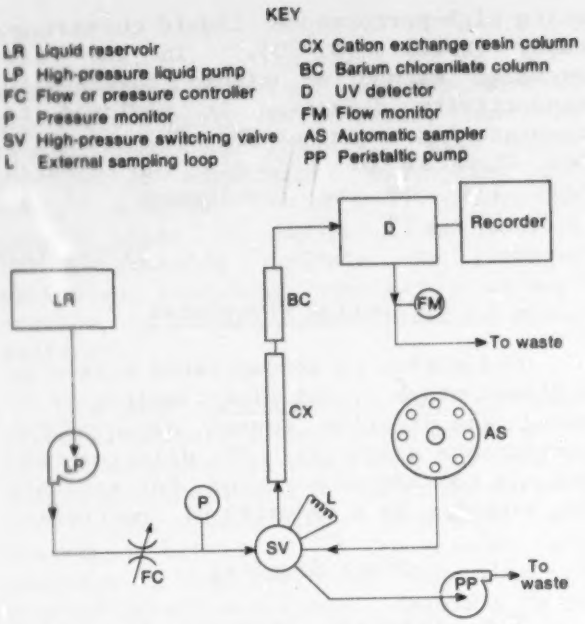

FIGURE 1. - Schematic of EPA automated column chloranilate instrument for determination of sulfate.

The Bureau's system, shown in figure 2, uses a manual sampling valve, Rheodyne Model 7120, that provides for syringe injection and is equipped with a 20- l sampling loop. The other components, employed as part of a Nester Faust Model 1240 liquid chromatograph, are a Milton Roy pump with a maximum pressure of 1,000 psig; a thermal degassing system for elution solvent; and a Chromatronics UV analyzer. The 254-nm filter within the cell compartment was replaced by a 310 nm ± 17 nm interference filter taped over the inlet aperture. The cation exchange resin generally used can be a commercial, strong-acid exchange resin in the hydrogen form. We did not use it in validating our method, since extraneous cations generally exist at low levels in diesel exhaust. In addition, a short length of activated charcoal is employed at the head of our column to lower the aromatic hydrocarbon UV blank.

A 7.5-cm by 0.625-cm-OD stainless steel column is washed with solvents or cleaned by filling with dilute detergent and treating in an ultrasonic bath.

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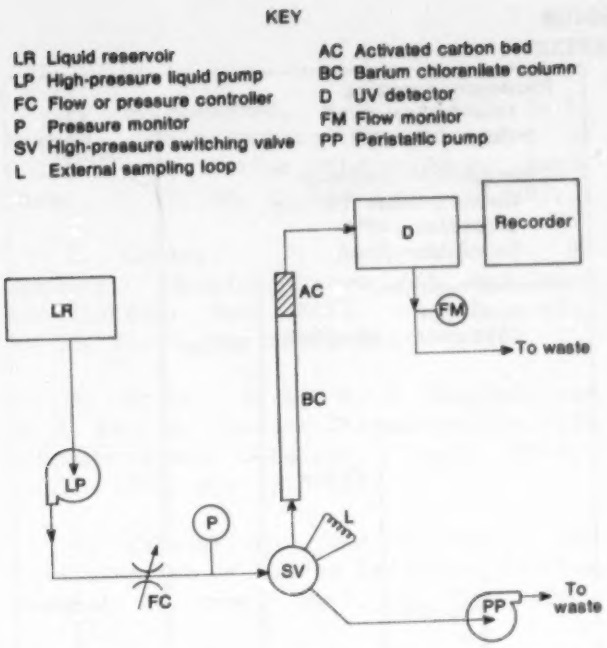

FIGURE 2. - Bureau modification of EPA column chloranilate instrument.

Barium chloranilate (25 g) is mixed with 15 ml of i.p. in a small beaker, and the latter is agitated in an ultrasonic bath for 5 min, allowed to stand 5 min, and the fines decanted. The process is repeated twice, and the mixture is filtered, followed by drying the chloranilate in an oven at 100° C. The cleaned column is then dry-packed with this material to within 3 cm of the top and covered with a thin layer of glass wool. Activated charcoal, minus 60 plus 80 mesh, is packed on top, and the column is terminated with wool or mesh.

The mobile phase mixture (600 ml i.p. per liter of H_2O) is degassed at 40° C. The pump is adjusted to provide a flowrate of 3 ml/min. A pressure of above 750 psig should result using the chloranilate column described. The sample loop is filled and sample injected. The chromatogram is recorded at a span of 1 mv.

Tandem Column Ion Exchange Procedure

The method described by Small (12) covers a wide variety of anions and cations and provides specific information. The anionic procedure, which includes sulfate, is described briefly below.

A strong-base anion exchange, such as Dowex 1, is ground finely, the powder is suspended in water, and most of the particles are allowed to settle, leaving an extremely fine supernatant liquid. A resin of very low exchange capacity is prepared by surface sulfonation of a styrene divinyl benzene (DVB) copolymer (2 pct DVB) accomplished by treatment with H_2SO_4 at 100° C. Typically, 10 g of resin is heated with 10 g of acid for 10 min. This provides a cation resin of about 0.02 meq/g. This product is contacted with an excess of the fine supernatant liquid, yielding complete surface coverage by agglomeration. The final product is anionic and is employed as the separating resin by dry-packing a 25-cm by 2-mm-ID glass microbore column. The stripper resin used in the tandem column is an ordinary strong-acid cation exchanger packed in a column twice the length. The latter is periodically regenerated with 0.25N H_2SO_4. The eluent recommended by Small is sodium phenoxide, 0.01 to 0.005N. Sodium bicarbonate and citrate can also be used in even lower concentrations.

An automated chromatograph specially designed for tandem column ion exchange along with the appropriate columns can be used by those in possession of the Dionex chromatograph designed specifically for this procedure.

Fritz (3) describes a procedure for cation chromatography using low-capacity resins, eliminating the need for a suppressor column. The paper also cites previous work on similar anion chromatography. In contrast to other ion detectors, sufficient sensitivity and balancing-out of background conductance is accomplished by the Wescan Conductivity Detector, Model 213.[7]

[7]Available from Wescan Instrument, Inc., 3018 Scott Boulevard, Santa Clara, Calif. 95050.

DISCUSSION

Collection Procedures

Statistics for collection accuracy and precision were not calculated since sufficient data were difficult to obtain. A very detailed description of the controlled condensation sampling procedure is given in the ORF report (9), but no data are given for precision and accuracy. However, in general, adequate statistics are furnished for chemical methods employed for collected samples.

Chemical Methods

The batch chloranilate method using 80 pct i.p. appears to have a limited range. In the Bureau's experiments Beer's law is followed up to about 80 ppm (w/v). More concentrated solutions are diluted with 80 pct i.p. to bring them within range. This is, of course, a significant limitation. However, this method is the easiest to implement, particularly for a few samples, equipment costs much less, and the procedure has the advantage of simplicity. Correlation coefficients in excess of 0.99 were obtained within the range.

In its automated column chloranilate procedure, EPA used a dilution tunnel for sample collection and an absorbance range of 0.002 full scale. Precision in the 0- to 50-ppm range is of the order of ±1 pct standard deviation. Recovery of pure H_2SO_4 added in known quantities to Fluoropore filters is excellent. Fluoropore (Teflon) filters are, however, difficult to work with mainly because of flowrate limitation.

In the Bureau's column chloranilate procedure, direct tailpipe samples are taken and it is difficult to make even a rough estimate of sampling precision or accuracy. In standardization tests, however, good accuracy and precision are obtained in the 0- to 100-ppm (v/v) range for the chemical method. Chromatographs of several sulfate standard samples are shown in figure 3. A regression calculation of the values presented in

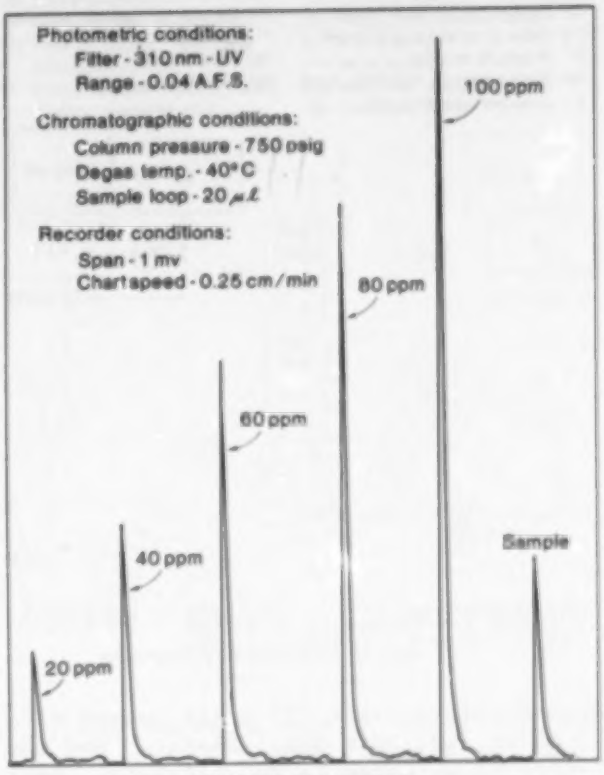

FIGURE 3. - Sequential peak response for sulfate standards. A.F.S. = absorbance, full-scale.

the figure 3 shows a correlation coefficient of 0.991 and a standard error of estimate, Sy/x, of ±0.8443. Some nonlinearity may occur below the lowest point, as alluded to by Tejada (14), but this is not very significant within the working range used (A = 0.04 full scale).

The method of choice is ion exchange for sulfate analysis, in general. It has good dynamic range and is sensitive (better than 0.1 ppm). Organic compounds do not interfere as they can in ultraviolet absorption techniques. Interferences, however, can arise from unseparated ions. For example, formate does not separate from acrolate, according to A. D. Little (6). However, in most cases, the most significant separations can be made ($SO_4^=$, NO_2, NO_3, Cl).

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